Cyclopentadienyl and Indenyl Complexes of Rhodium(I) and Rhodium(III) Containing Chiral Diphosphines. X-ray Structure of $(R)_C,(S)_{Rh}$-$[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]BPh_4$

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Cyclopentadienyl and indenyl complexes of the type $(\eta^5\text{-}C_5H_5)Rh(L_2)$ and $(\eta^5\text{-}C_9H_7)Rh(L_2)$ (L_2 = chiral diphosphine) have been synthesized and characterized through multinuclear NMR spectroscopy. These formally planar complexes react with methyl iodide to give the pseudotetrahedral methyl derivatives $[(\eta^5\text{-}C_5H_5)Rh(CH_3)(L_2)]I$ and $[(\eta^5\text{-}C_9H_7)Rh(CH_3)(L_2)]I$. The stereochemistry of these complexes, as far as the stereogenic metal center is concerned, is inferred by the difference of chemical shifts of the two phosphorus atoms in the ^{31}P NMR spectra of the diastereomeric pairs. The crystal structure of $(R)_C,(S)_{Rh}$-$[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]BPh_4$ has been determined and confirms the above assignment. The electrochemical reduction of the same complex is interpreted in terms of a charge-transfer process followed by the homolytic fission of the Rh–CH_3 σ-bond of the electrogenerated rhodium(II) complex.

Introduction

In the course of our research dealing with the stereochemistry of simple organometallic reactions related to catalysis by transition-metal complexes, we have been interested in the synthesis, characterization, and stereochemical behavior of organometallic complexes of ruthenium(II) and rhodium(I) containing cyclopentadienyl and indenyl ligands and chiral diphosphines.[1,2] These complexes have basic properties[3] and have potential as chiral catalysts; furthermore, they can be used as templates for stereospecific transformations of organic ligands.[4] We reported preliminary results on the synthesis and on the dynamic behavior in solution of new complexes of rhodium(I) of general formula $[(\eta^5\text{-}C_9H_7)Rh(L_2)]$ (L_2 = chiral diphosphines)[2] and on their reactivity toward methyl iodide to form the corresponding $[(\eta^5\text{-}C_9H_7)Rh(CH_3)(L_2)]I$ products.[5] The use of chiral diphosphines having C_1 symmetry enables us to evaluate the stereochemical bias displayed by these ligands on the incoming electrophile in the formation of pseudotetrahedral complexes starting from formally planar molecules.[6] This kind of reaction can be considered as the organometallic counterpart of the diastereoface-differentiating reactions which can take place at the trigonal carbon atom.[7]

In this paper we report in detail on the preparation and characterization of the complexes $(\eta^5\text{-}C_5H_5)Rh(L_2)$ and $(\eta^5\text{-}C_9H_7)Rh(L_2)$[2] and their reactivity with CH_3I and other electrophiles. A simple empirical rule based on the difference of chemical shift of the phosphorus atoms of the used diphosphines in the $^{31}P\{^1H\}$ NMR spectra for the determination of the absolute configuration at the stereogenic metal center in rhodium(III) complexes containing C_1 diphosphines is also given. This correlation finds support in the determination of the X-ray structure of the complex $(R)_C,(S)_{Rh}$-$[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]BPh_4$.

Results and Discussion

Preparation and Spectroscopic Properties. The cyclopentadienyl complexes $(\eta^5\text{-}C_5H_5)Rh(L_2)$ (1) were prepared by reacting $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$ with an equimolar amount of the appropriate diphosphine in toluene at reflux for about 6 h. The corresponding indenyl complexes 3, whose preparation and multinuclear NMR characterization were recently reported,[2] were prepared by treatment at room temperature of $(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2$ with the diphosphines in toluene. This rate enhancement has generally been attributed to a facile ring slippage of the indenyl ligand from η^5- to η^3-bonding mode in a associative transition state.[8] The cyclopentadienyl complexes were

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(3) Werner, H. *Angew. Chem.* **1983**, *95*, 932.
(4) For possible developments in this field compare: (a) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1. (b) Davies, S. G. *Pure Appl. Chem.* **1988**, *60*, 13. (c) Dalton, D. M.; Fernàndez, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9198.
(5) Morandini, F.; Consiglio, G. *J. Chem. Soc., Chem. Commun.* **1991**, 676.
(6) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interaction in Chemistry*; Wiley: New York, 1985; pp 366-372.
(7) Seebach, D.; Prelog, V. *Angew. Chem.* **1982**, *94*, 696.
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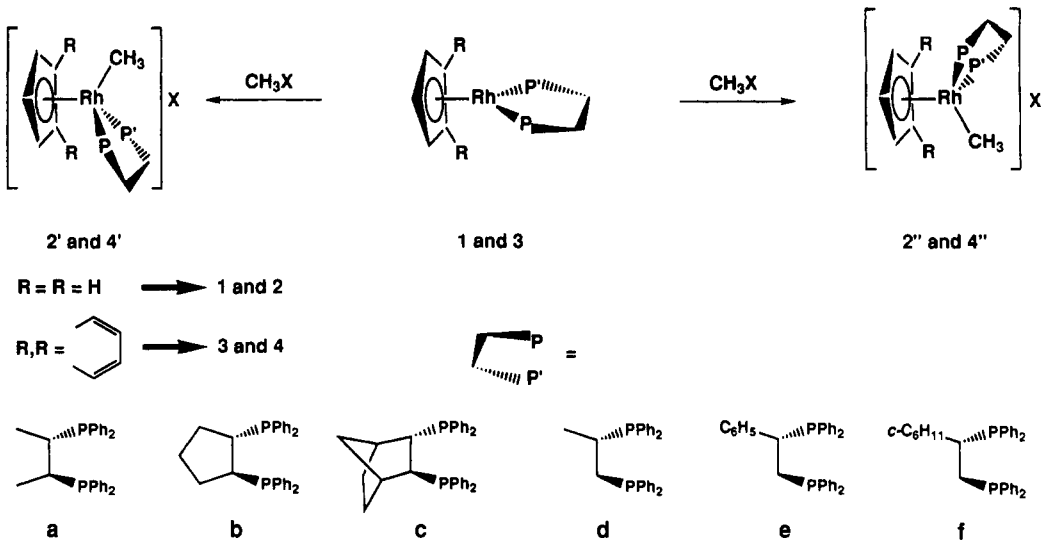
Scheme I



characterized through elemental analysis and multinuclear NMR spectroscopy (^{1}H, ^{31}P, and ^{13}C NMR).

The ^{1}H NMR spectra of the complexes show, in addition to the resonances of the various diphosphines used, signals due to the cyclopentadienyl protons as a singlet in the range δ 4.8–5.1.

The ^{31}P{^{1}H} NMR spectra of the complexes containing the diphosphines having C_2 symmetry consist of the expected doublet arising from the coupling of the two phosphorus atoms with the ^{103}Rh nucleus. When chiral ligands having C_1 symmetry are present, an eight-line pattern arising from nonequivalent phosphorus atoms coupled with ^{103}Rh is observed. The spectra are temperature-independent to 173 K.

In contrast, the corresponding indenyl complexes show a fluxional behavior in the same range of temperature.[2] This fluxionality was ascribed to the rotation of the indenyl ligand around the rhodium–indenyl bond axis, which is slowed down as the temperature is lowered. Normally the coordination geometry around the metal atom in such complexes can be considered "pyramidal" rather than "planar"[6,9] (vide infra). Therefore, the fluxional behavior might be ascribed to a rapid inversion at the stereogenic rhodium atom[2] similar to that well-known for EX_3 (E = group 15 element) compounds.[10] This inversion should, however, occur at much lower temperature for analogous complexes containing the cyclopentadienyl ligand.

The ^{13}C NMR spectra show resonances due to the cyclopentadienyl carbon atoms, being in the range 84–88 ppm.

Reaction with Electrophiles. The complexes (η^5-C_5H_5)Rh(L_2) (**1**) and (η^5-C_9H_7)Rh(L_2) (**3**) react rapidly (about 5 min) with CH_3I in dichloromethane solution to give the corresponding cationic methyl derivatives [(η^5-C_5H_5)Rh(L_2)(CH_3)]I (**2**) and [(η^5-C_9H_7)Rh(L_2)(CH_3)]I (**4**), respectively. When diphosphines having C_1 symmetry are used, two diastereomers can form (Scheme I). The values of chemical shifts and coupling constants for the ^{1}H, ^{31}P, and ^{13}C spectra are in agreement with the proposed structures.

For the indenyl complexes, the three protons of the five-membered ring lie in the range δ 6.1–5.7, whereas signals for the corresponding cyclopentadienyl complexes are between δ 5.0 and 5.6. In both cases the values of chemical shift are at lower field when compared with those found for the complexes of rhodium(I), in keeping with the lower electron density at the metal atom. Moreover, the signals due to the cyclopentadienyl protons appear in general as a triplet, probably due to the coupling with the two phosphorus atoms of the diphosphine.

Table I. Diastereoselectivity[a] in the Formation of Complexes 2 and 4 from 1 and 3

	c	d	e	f
2 (X = I)	41:59	100:0	85:15	100:0
4 (X = I)	55:45	100:0	86:14	100:0
4 (X = *p*-toluenesulfonate)		95:5	81:19	
4 (X = trifluoromethanesulfonate)		95:5	79:21	

[a] Ratio of diastereomers having the larger difference in chemical shifts of the ^{31}P NMR signals to diastereomers with the smaller difference.

The ^{13}C chemical shifts of the carbon atoms of the five-membered ring of the indenyl ligand lie between 70 and 90 ppm, the resonances due to the other carbon atoms being in the region of those of the phenyl groups. According to a previous report, this indicates η^5 coordination of the indenyl ligands for all the complexes.[11]

The complexes containing diphosphines having C_2 symmetry show in the ^{31}P NMR spectra a doublet of doublets for each of the diastereotopic phosphorus atoms. When diphosphines having C_1 symmetry are used, as in the case of phenphos (**e**) or renorphos (**c**), the spectra show the presence of the two possible diastereomers **4′/4″** in ratios of 86/14 and 55/45 and **2′/2″** in ratios of 85/15 and 41/59, respectively. In the case of complexes containing prophos (**2d** and **4d**) or cycphos (**2f** and **4f**) ligands, only one of the two possible diastereomers is observed[5] (Table I).

These ratios remain practically unchanged when other methylating agents are employed, such as methyl trifluoromethanesulfonate or methyl *p*-toluenesulfonate. In the reaction of **3d** the major diastereomer is overwhelmingly formed (**4′d/4″d** = *ca.* 20), only a trace amount of the alternative diastereomer being recognizable in the ^{31}P NMR spectrum. For **3e** again diastereomeric ratios **4′e/4″e** of about 4 were obtained.

We attempted to change the diastereomeric composition (**4′e/4″e**) (6.1/1 diastereomeric ratio) obtained for the complex [(η^5-C_9H_7)Rh($Ph_2PCH(C_6H_5)CH_2PPh_2$)(CH_3)]I

(9) Hofmann, P. *Angew. Chem.* **1977**, *89*, 551.
(10) Levin, C. C. *J. Am. Chem. Soc.* **1975**, *97*, 5649.
(11) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839.

by treatment with a small amount (~10%) of sodium amalgam (Na/Hg) in acetonitrile in a temperature range between −50 and +30 °C.[12] However, no change in the diastereomeric composition was evident through $^{31}P\{^1H\}$ NMR spectroscopy in CD_2Cl_2 on the product recovered after filtration of the amalgam, evaporation of the solvent under vacuum, and dissolution of the residue. Similarly, the diastereomeric ratio remained unchanged on heating at reflux the same complex for 4 days directly in an NMR tube in acetonitrile-d_3. When the solution was monitored from time to time, no epimerization of the starting diastereomer was evident, only a small amount of decomposition products being formed.

Similar experiments were carried out on the diastereomerically pure complex $[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]BPh_4$ obtained from the corresponding iodide **4d** through metathesis with $NaBPh_4$. In this case as well no evidence of epimerization was observed. Also unsuccessful were attempts to epimerize the same complex through electrocatalytic cyclovoltammetry and/or controlled-potential coulometry experiments in acetonitrile–tetraethylammonium perchlorate (0.2 M) solution. These tests have shown that a fugitive rhodium(II) species is reversibly formed (vide infra) at the electrode ($t_{0.5} \approx 0.15$ s at −20 °C). However, this intermediate seems to be too short-lived to undergo rearrangement capable of promoting epimerization of the depolarizer. In fact, if the catholyte is dried under vacuum and the residue dissolved in dichloromethane, the $^{31}P\{^1H\}$ NMR spectrum shows only the presence of the starting diastereomer.

We have also tested the reactivity of *i*-C_3H_7I and *sec*-C_4H_9I with the rhodium(I) complexes in different solvents such as dichloromethane, dimethyl sulfoxide, and acetonitrile. In all cases, no reaction was observed, even at high temperature. The rhodium(I) complexes can probably react with CH_3I as a nucleophile with an S_N2 mechanism. The lack of reactivity of *i*-C_3H_7I and *sec*-C_4H_9I can be explained on the basis of steric reasons.

The $^{31}P\{^1H\}$ NMR spectra of the complexes $[(\eta^5\text{-}C_9H_7)Rh(phenphos)(CH_3)]I$, $[(\eta^5\text{-}C_9H_7)Rh(renorphos)(CH_3)]I$, and $[(\eta^5\text{-}C_9H_7)Rh(prophos)(CH_3)]X$ (X = trifluoromethanesulfonate or *p*-toluenesulfonate), in which the two possible diastereomers are both recognized, show a further peculiarity. In fact, in these cases the peaks due to the minor diastereomer fall within those relative to the major diastereomer. The same trend was observed for the $[(\eta^5\text{-}C_5H_5)Ru(L_2)X]$ (X = Cl, H, CH_3, $SnCl_3$) complexes, for which the absolute configuration at the metal center is known.[1] In fact, the *ul* diastereomer having the $(S)_{Ru},(R)_C$ configuration exhibits differences in the ^{31}P chemical shifts for the two phosphorus atoms which are always larger than those for the $(R)_{Ru},(R)_C$ diastereomer. Furthermore, with only two exceptions, the ^{31}P resonances of the $(R)_{Ru},(R)_C$ diastereomer fall within the resonances corresponding to the $(S)_{Ru},(R)_C$ diastereomers. Therefore, it was suggested[1] that the difference in the ^{31}P chemical shifts could give an indication of the absolute configuration at the metal center. If we assume that this empirical correlation is valid also for isostructural and isoelectronic rhodium complexes, than the absolute configuration of the rhodium atom in the diastereomers having larger separation of ^{31}P chemical shift is *S*. A comparison of the differences in the chemical shifts for the two diastereomers of the phenphos derivatives (~20 ppm vs ~5 ppm) with those observed for the single diastereomer formed in the case of the prophos and the cycphos ligand (26–30 ppm) suggests the same absolute configuration (*S*) at the metal atom for these compounds. This assignment is in fact confirmed by the crystal structure determination of $(R)_C,(S)_{Rh}$-$[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]BPh_4$ (vide infra).

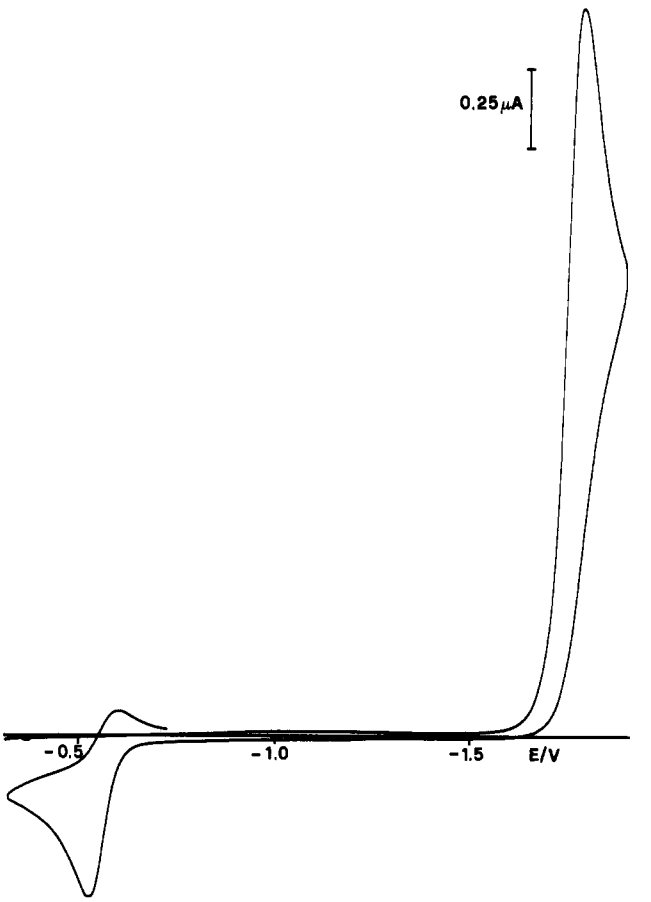


Figure 1. Cyclic voltammogram for reduction of 1.85 mM of $[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]BPh_4$ in AN (0.2 M TEAP) at 25 °C (scan rate 0.2 V s^{-1}).

The prevailing formation of the *ul* diastereomer[7] can again be understood on the basis of steric reasons, i.e. a prevailing attack of the electrophile at the metal from the direction opposite to that of the substituent on the chelate ring of the diphosphine ligand.

Electrochemistry. The electrochemical reduction of the complex $[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]BPh_4$ in acetonitrile–tetraethylammonium perchlorate (0.2 M) solution at 25 °C occurs in a single one-electron irreversible and diffusion-controlled step. However, the characteristics of the cyclic voltammetry (CV) pattern (Figure 1), *i.e.* (i) the shape of the cathodic peak ($E_{p/2} - E_p^c = 50$ mV), (ii) the dependence of E_p^c on scan rate, v, ($\Delta E_p^c/\Delta \log v = 30$ mV), (iii) the $i_p i^{-1/2}$ value independent of v in a wide range of scan rates, and (iv) the appearance of a coupled oxidation peak at far more anodic potentials ($E_p^a - E_p^c = 1.28$ V), suggest that the apparent irreversibility may conceal an EC mechanism, *i.e.* an essential Nernstian one-electron reduction followed by a fast irreversible chemical reaction. Indeed, CV tests carried out at lower temperatures (−20 °C) show for scan rates between 0.4 and 10 V s^{-1} the appearance and growing on the reverse scan of the reversibly coupled anodic peak attributable to the back-oxidation of the fugitive rhodium(II) derivative. A fully developed redox couple ($i_p^a/i_p^c = 1$) centered at $E^\circ = -1.84_5$ V vs $FeCp_2^+/FeCp_2$ is thus

(12) Brunner, H.; Fisch, K.; Jones, P. J.; Salbeck, J. *Angew. Chem.* **1989**, *101*, 1558.

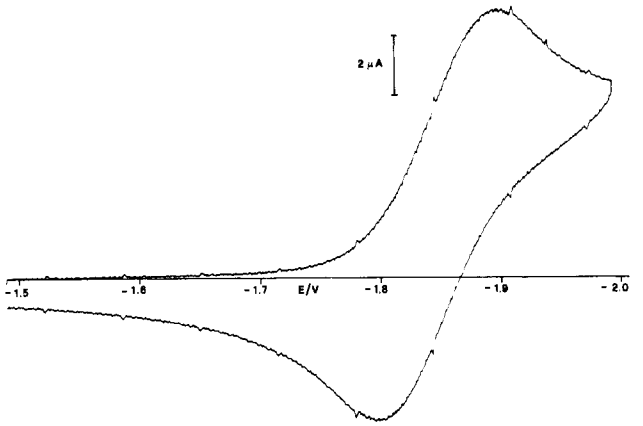


Figure 2. Cyclic voltammogram for reduction of 1.85 mM of $[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]BPh_4$ in AN (0.2 M TEAP) at −20 °C (scan rate 10 V s^{-1}).

apparent for $v \geq 10$ V s^{-1} (Figure 2). This allowed the kinetics of chemical reaction to be studied by CV, in which the ratio of anodic to cathodic peak currents, i_p^a/i_p^c, was measured as a function of scan rate and depolarized concentration. The data were found to fit satisfactorily the theory developed for a first-order chemical reaction following charge transfer[13] and gave a rate constant of 4.5 ± 0.5 s^{-1} at −20 °C. Exhaustive controlled-potential electrolysis carried out at 25 °C and at potentials past the cathodic peak confirms the uptake of a single electron per molecule of the depolarizer and leads to a brown solution whose voltammogram shows a reversible one-electron-oxidation process centered at $E° = -0.56_0$ V, already evident in the cyclic voltammogram of the rhodium(III) precursor on the reverse scan (Figure 1). The brown product, recovered from the spent catholyte upon evaporation of the solvent under reduced pressure and subsequent extraction with toluene followed by addition of *n*-hexane, was identified as the $(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)$ complex by ^1H and ^{31}P NMR spectroscopy. Its identity was substantiated by the restoration of the starting methyl derivative rhodium(III) cation complex upon reaction with CH_3I.

Hence, the chemical reaction following the charge-transfer process has to be recognized in the homolytic fission of the Rh–CH_3 σ-bond in the electrogenerated rhodium(II) complex. Related behavior has already been found in Vaska-type organometallic iridium complexes.[14]

Crystal Structure of $(R)_C,(S)_{Rh}$-$[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]BPh_4$. The crystal structure of the title compound consists of the packing of $[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]^+$ cations and BPh_4^- anions separated by normal contacts. There are two independent cations (and anions) in the asymmetric unit. Parts a and b of Figure 3 report ORTEP drawings of the two cations (A and B) in their absolute configuration $(R)_C,(S)_{Rh}$. Relevant bond parameters are reported in Tables II and III. The coordination around the Rh atom may be regarded as octahedral, with one face of the octahedron occupied by the methyl and the diphosphine ligands and the opposite one by the indenyl ligand, like that found in the $[(\eta^5\text{-}C_5Me_5)Rh(H)(PPh_3)_2]^+$ cation, which has a somewhat related geometry.[15] The Rh–C_{Me}

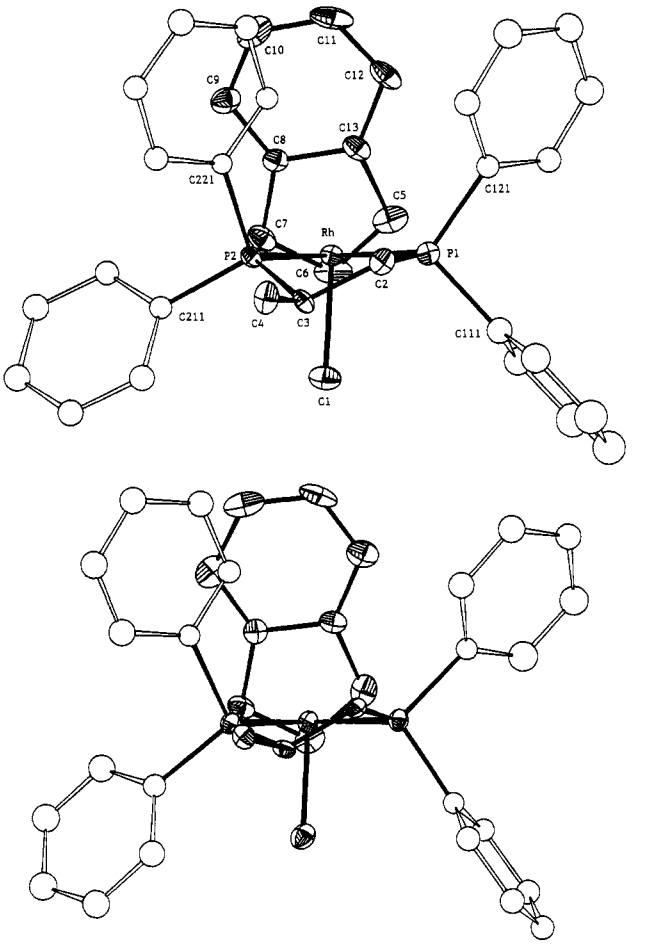


Figure 3. Molecular structure and numbering scheme of the cation of $(R)_C,(S)_{Rh}$-$[(\eta^5\text{-}C_9H_7)Rh(Ph_2PCH(CH_3)CH_2PPh_2)(CH_3)]BPh_4$: (a, top) molecule A; (b, bottom) molecule B.

Table II. Bond Distances (Å)

	molecule A	molecule B		molecule A	molecule B
Rh–P1	2.284(3)	2.272(4)	P2–C221	1.815(7)	1.825(9)
Rh–P2	2.263(3)	2.265(3)	C2–C3	1.52(2)	1.53(2)
Rh–Cl	2.12(1)	2.09(1)	C3–C4	1.54(2)	1.57(1)
Rh–C5	2.23(2)	2.21(1)	C5–C6	1.37(2)	1.37(3)
Rh–C6	2.20(2)	2.20(2)	C5–C13	1.44(2)	1.43(2)
Rh–C7	2.23(2)	2.22(2)	C6–C7	1.40(3)	1.42(2)
Rh–C8	2.37(1)	2.42(2)	C7–C8	1.43(2)	1.46(2)
Rh–C13	2.36(1)	2.39(2)	C8–C9	1.39(2)	1.38(2)
P1–C2	1.82(1)	1.83(1)	C8–C13	1.42(2)	1.43(2)
P1–C111	1.82(1)	1.821(8)	C9–C10	1.32(2)	1.39(3)
P1–C121	1.831(8)	1.807(9)	C10–C11	1.37(3)	1.37(3)
P2–C3	1.84(1)	1.84(1)	C11–C12	1.38(3)	1.35(3)
P2–C211	1.808(8)	1.79(1)	C12–C13	1.41(2)	1.39(3)

(average 2.10 Å) bond distances are consistent with the data found in the literature for such an interaction (mean value 2.09(3) Å),[16] and the methyl is slightly bent toward P2 (C1–Rh–P2 = 84.7°), *i.e.* toward the most "equatorial" of the phenyl rings (vide infra), as also occurred for the chlorine ligand in the $[(\eta^5\text{-}C_9H_7)RuCl(PPh_2CH(CH_3)CH(CH_3)PPh_2)]$ complex.[17] The Rh–P (mean 2.271 Å) bond lengths agree with those found in analogous complexes with chelating diphosphines such as $[Rh(COD)(PPh_2CH(CH_3)CH(CH_3)PPh_2)]^+$ (Rh–P = 2.270 Å (mean) and P–Rh–P = 83.82(6)°)[18] and [Rh(norbornadiene)(PPh_2CH_2-

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(15) Mingos, D. M. P.; Minshall, P. C.; Hursthouse, M. B.; Malik, K. M. A.; Willoughby, S. D. *J. Organomet. Chem.* **1979**, *181*, 169 (crystallized as the PF_6^- salt).
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(17) Morandini, F.; Consiglio, G.; Sironi, A.; Moret, M. *J. Organomet. Chem.* **1989**, *370*, 305.

Table III. Bond and Torsion Angles (deg)

	molecule A	molecule B
	Bond Angles	
P1–Rh–P2	84.8(1)	85.6(1)
C1–Rh–P1	90.6(4)	89.7(4)
C1–Rh–P2	84.7(4)	84.5(3)
P1–Rh–In*	131.8(1)	131.8(1)
P2–Rh–In*	131.9(1)	132.2(1)
C1–Rh–In*	118.5(3)	118.2(4)
C2–P1–Rh	107.3(4)	107.9(4)
C111–P1–Rh	117.1(3)	115.5(3)
C111–P1–C2	106.4(5)	107.0(4)
C121–P1–Rh	116.0(3)	117.4(3)
C121–P1–C2	107.2(4)	105.7(5)
C121–P1–C111	102.2(4)	102.5(4)
C3–P2–Rh	107.5(4)	107.7(3)
C211–P2–Rh	115.9(3)	115.1(3)
C211–P2–C3	108.8(4)	108.0(5)
C221–P2–Rh	116.9(3)	115.9(3)
C221–P2–C3	103.2(4)	104.1(5)
C221–P2–C211	103.7(4)	105.4(4)
C3–C2–P1	114.3(7)	110.0(8)
C2–C3–P2	105.1(8)	107.6(8)
C4–C3–P2	117.7(9)	115.0(8)
C4–C3–C2	110.3(9)	112(1)
C13–C5–C6	110(2)	110(1)
C7–C6–C5	109(1)	108(2)
C8–C7–C6	108(1)	107(1)
C9–C8–C7	132(1)	134(1)
C13–C8–C7	108(1)	107(1)
C13–C8–C9	120(1)	119(1)
C10–C9–C8	119(2)	119(2)
C11–C10–C9	122(2)	122(2)
C12–C11–C10	123(1)	120(2)
C13–C12–C11	117(2)	120(2)
C8–C13–C5	106(1)	107(1)
C12–C13–C5	135(2)	134(1)
C12–C13–C8	119(1)	120(1)
	Torsion Angles	
Rh–P1–C2–C3	25.0(9)	36.5(8)
P1–C2–C3–P2	–45.8(10)	–50.1(9)
C2–C3–P2–Rh	46.9(8)	42.3(8)
C3–P2–Rh–P1	–26.6(4)	–16.1(4)
P2–Rh–P1–C2	4.2(4)	–8.0(4)
P2–Rh–P1–C111	123.5(4)	111.8(4)
P2–Rh–P1–C121	–115.6(4)	–127.1(4)
P1–Rh–P2–C211	–148.5(4)	–136.6(4)
P1–Rh–P2–C221	88.64(4)	99.9(4)
Rh–P1–C111–C112	31.5(9)	51.5(7)
Rh–P1–C111–C116	–149.2(7)	–130.6(6)
Rh–P1–C121–C122	–82.7(6)	–79.8(7)
Rh–P1–C121–C126	89.2(7)	97.5(7)
Rh–P2–C211–C212	110.0(7)	102.6(7)
Rh–P2–C211–C216	–70.5(7)	–69.5(7)
Rh–P2–C221–C222	–22.2(8)	–29.9(8)
Rh–P2–C221–C226	160.9(6)	154.3(6)

$CH(C_6H_{11})PPh_2)]^+$ (Rh–P = 2.29 Å (mean) and P–Rh–P = 84.1° (mean)),[19] while the P–Rh–P (mean 85,2°) "bite" angles are slightly larger than in the above-cited cations. The indenyl ligand is η^5-coordinated to the metal atom; the Rh–C interactions involving the bridgehead carbon atoms are longer than the other carbon–metal bonds within the η^5 moiety, thus indicating an incipient $\eta^5 \rightarrow \eta^3$ distortion. This feature is normal for η^5-indenyl complexes,[20] and the amount of the distortion can be quantified either by the folding of the allylic plane with respect to the least-squares plane of the six-membered ring (8.2 and 11.2° for the A and B molecules, respectively) or by the slippage of the coordinated ring (0.18 and 0.23 Å for A and B molecules, respectively) as defined by Faller et al.[20]

(18) Ball, R. G.; Payne, N. C. *Inorg. Chem.* **1977**, *16*, 1187 (crystallized as the ClO_4^- salt, containing clathrate THF).
(19) Oliver, J. D.; Riley, D. P. *Organometallics* **1983**, *2*, 1032 (crystallized as the ClO_4^- salt).
(20) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929.

Table IV. Summary of Crystal Data and Data Collection/Analysis Parameters for $(R)_C,(S)_{Rh}$-$[(\eta^5\text{-}C_9H_7)Rh(CH_3)(prophos)][BPh_4]$

formula	$C_{61}H_{56}BP_2Rh$
M_r	964.79
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
a/Å	14.360(2)
b/Å	11.888(6)
c/Å	28.687(6)
β/deg	95.66(2)
V/Å^3	4874(4)
Z	4
D_c/g cm^{-3}	1.315
$F(000)$	2008
cryst dimens/mm	0.15 × 0.10 × 0.07
μ(Mo Kα)/cm^{-1}	4.5
min rel transmissn factor	0.95
no. of rflns for ψ scan	3
θ range/deg	3–24
scan mode	ω
scan range/deg	0.8 + 0.35 tan θ
required $\sigma(I)/I$	0.01
max scan time/s	70
octants of recipr space collected	$\pm h,k,l$
cryst decay/%	6
no. of collected rflns (at room temp)	8573
no. of unique obsd rflns ($I > 3\sigma(I)$)	4073
no. of refined params	488
weights	$1.5317/(\sigma^2(F_o) + 0.000325F_o^2)$
max shift/error	<0.01
R^a	0.0462
R'^b	0.0437
max peak diff Fourier map/e Å^{-3}	0.49

^{a} $R = \Sigma(|F_o - k|F_c||)/\Sigma F_o$. ^{b} $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]$.

The two cations have (slightly) different stereogeometries, the $Rh(Ph_2PCH(CH_3)CH_2PPh_2)$ metallacycle conformation being closer to flap in A and skew in B. The differences in the rings have some influence on the rotameric conformations, i.e. the face-edge exposure described by the Rh–P–C_{ipso}–C_{ortho} angles, and on the axial/equatorial character (described by the P–Rh–P–C_{ipso} angles) of the phenyl groups, and the pertinent dihedral angles are reported in Table II. The two conformers share, nevertheless, the absolute configuration (λ) of the metallacycle because, as previously observed, the methyl avoidance for the crowded axial position binds the *R/S* prophos absolute configuration to the λ/δ metallacycle conformation.

Experimental Section

Structure Determination and Refinements. A transparent yellow crystal of dimensions 0.15 × 0.10 × 0.07 mm was mounted on an Enraf-Nonius CAD-4 diffractometer, and 25 intense reflections having a θ value in the range 10.0–14.0° were centered using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Least-squares refinement of their setting angles resulted in the unit-cell parameters reported in Table IV, together with an orientation matrix relating the crystal axes to the diffractometer axes. A total of 8573 diffracted intensities (4073 with $I > 3\sigma(I)$) were collected at room temperature with variable scan speed (maximum scan time for each reflection 70 s), by exploring the quadrant of the reciprocal lattice with $-16 \le h \le 16$, $0 \le k \le 13$, and $0 \le l \le 32$, out to a maximum 2θ angle of 48°.

Intensity was checked by monitoring three standard reflections every 60 min. Final drift corrections where between 0.99 and 1.06. The diffracted intensities were corrected for Lorentz, polarization, and background effects. An empirical absorption correction was applied according to the method developed by North *et al.*[21] based on ψ scans (ψ = 0–360°, every 10°) of three reflections having χ values near 90°.

(21) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

Scattering factors for neutral atoms and anomalous dispersion corrections for scattering factors were taken from refs 22 and 23, respectively.

The positions of the two independent rhodium atoms were determined from a three-dimensional Patterson function. The coordinates of the remaining non-hydrogen atoms were located by successive least-squares refinements and Fourier difference maps.

Block-matrix least-squares was based on F, the maximized function being $\sum w(F_o - k\|F_c\|)^2$. Weights assigned to individual observations are described in Table IV. Anisotropic thermal parameters were assigned to all atoms but those belonging to phenyl groups, which were treated as rigid bodies of D_{6h} symmetry (C–C = 1.395 Å). Hydrogen atoms were placed in idealized positions (C–H = 0.95 Å) and refined riding on their parent atom with fixed isotropic thermal parameters (B = 6.0 Å^2). The absolute configuration was determined by internal comparison and subsequently confirmed by refining the two possible enantiomers. The final values of the agreement indices, R and R', for the best and, in parentheses, for the worst enantiomeric choice were 0.0462 (0.0467) and 0.0437 (0.0444), respectively. The final positional parameters are reported in Table V. The maximum residual in the final difference Fourier synthesis was 0.5 e/Å^3.

All the calculations were performed on a Personal IRIS 35 computer using SHELX.[24]

Materials. All reactions and manipulations were carried out under nitrogen. The solvents were dried and degassed before use. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR specra were recorded on a JEOL FX 90 Q or on a AM 400 Bruker spectrometer. Positive δ values in ppm are downfield from internal Me_4Si (^{1}H and ^{13}C) or external 85% H_3PO_4 (^{31}P).

Anhydrous acetonitrile (AN) was purchased from Aldrich and used as received. The electrolyte tetraethylammonium perchlorate (TEAP; C. Erba) was dried in vacuo at 75 °C prior to use. High-purity argon, further purified from oxygen by passage over reduced copper at 450 °C, was used in electrochemical experiments.

Cyclopentadiene was obtained from Aldrich and distilled before use. Indene (99%) was obtained from Aldrich, KH (20–25 wt % dispersion in mineral oil) was purchased from Jansen, and 1,2-bis(diphenylphosphino)ethane (dppe) and triphenylphosphine were obtained from Fluka and were used without purification. Methyl trifluoromethanesulfonate and methyl p-toluenesulfonate are from Aldrich.

rac-1,2-Bis(diphenylphosphino)cyclopentane (cypenphos),[25] (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane (chiraphos),[26] (*R*)-1,2-bis(diphenylphosphino)propane (prophos),[27] (*R*)-1-cyclohexyl-1,2-bis(diphenylphosphino)ethane (cycphos),[28] (*R*,*R*)-2-*exo*-3-*endo*-bis(diphenylphosphino)bicyclo[2.2.1]heptane (renorphos),[29] (*R*)-1-phenyl-1,2-bis(diphenylphosphino)ethane (phenphos),[30] (η^5-C_5H_5)Rh(C_2H_4)$_2$,[31] (η^5-C_9H_7)Rh(C_2H_4)$_2$,[32] and (η^5-C_5H_5)Rh(PPh_3)$_2$[33] were prepared according to published procedures. The synthesis and NMR characterization of indenylrhodium complexes were in part reported elsewhere.[2,5]

General Procedure for the Preparation of (η^5-C_5H_5)Rh(L_2) Complexes. A 0.3-g (1.34-mmol) amount of (η^5-C_5H_5)Rh(C_2H_4)$_2$ was reacted with a equimolar amount of the appropriate phosphine or diphosphine in 20 mL of toluene at reflux temperature. After 4 h the solvent was removed under reduced pressure and 20 mL of *n*-hexane was added to the residue. The orange microcrystalline compounds were filtered off, washed several times with *n*-hexane, and dried in vacuo. Recrystallization was from CH_2Cl_2/*n*-hexane. Yields are in the range 60–80%.

Elemental analyses and NMR parameters (δ, CD_2Cl_2) for the complexes are as follows.

(η^5-C_5H_5)Rh(chiraphos) (1a). ^{1}H NMR: 7.17 (m, 20H, C_6H_5); 4.81 (s, 5H, C_5H_5); 2.38 (m, 2H, CH); 1.06 (dd, J_{HH} = 6.8 Hz, J_{PH} = 14.2 Hz, 6H, CH_3). ^{31}P NMR: 83.6 (d, J_{RhP} = 212.4 Hz). ^{13}C NMR: 137.9–127.0 (m, C_6H_5); 85.4 (s, C_5H_5); 38.8–31.5 (m, CH); 15.1–12.0 (m, CH_3). Anal. Found: C, 66.23; H, 5.25. Calcd for $C_{33}H_{33}P_2Rh$: C, 66.37; H, 5.59.

(η^5-C_5H_5)Rh(cypenphos) (1b). ^{1}H NMR: 7.23 (m, 20H, C_6H_5); 4.91 (s, 5H, C_5H_5); 2.33–0.87 (m, 8H, CH + CH_2). ^{31}P NMR: 58.5 (d, J_{RhP} = 219.7 Hz). ^{13}C NMR: 143.6–127.5 (m, C_6H_5); 84.7 (s, C_5H_5); 40.1, 31.0, 24.0 (m, CH + CH_2). Anal. Found: C, 67.17; H, 5.56. Calcd for $C_{34}H_{33}P_2Rh$: C, 67.33; H, 5.48.

(η^5-C_5H_5)Rh(renorphos) (1c). ^{1}H NMR: 7.23 (m, 20H, C_6H_5); 4.91 (s, 5H, C_5H_5); 2.47–0.27 (m, 10H, CH + CH_2). ^{31}P NMR: 63.9 (dd, J_{PP} = 53.7 Hz, J_{RhP} = 224.6 Hz); 54.2 (dd, J_{PP} = 53.7 Hz, J_{RhP} = 222.2 Hz). ^{13}C NMR: 136.6–127.5 (m, C_6H_5); 84.4 (s, C_5H_5); 43.2, 36.6 (m, CH + CH_2). Anal. Found: C, 67.80; H, 5.68. Calcd for $C_{36}H_{35}P_2Rh$: C, 68.36; H, 5.57.

(η^5-C_5H_5)Rh(prophos) (1d). ^{1}H NMR: 7.22 (m, 20H, C_6H_5); 5.05 (s, 5H, C_5H_5); 2.46–1.76 (m, 3H, CH + CH_2); 0.71 (dd, J_{HH} = 6.8 Hz, J_{PH} = 12.2 Hz, 3H, CH_3). ^{31}P NMR: 89.3 (dd, J_{PP} = 51.3 Hz, J_{RhP} = 217.3 Hz); 70.8 (dd, J_{PP} = 51.3 Hz, J_{RhP} = 217.3 Hz). ^{13}C NMR: 135.8–127.2 (m, C_6H_5); 85.2 (s, C_5H_5); 39.5–33.3 (m, CH + CH_2); 16.8 (bs, CH_3). Anal. Found: C, 67.33; H, 5.46. Calcd for $C_{32}H_{31}P_2Rh$: C, 66.21; H, 5.38.

(η^5-C_5H_5)Rh(phenphos) (1e). ^{1}H NMR: 7.39 (m, 25H, C_6H_5); 5.09 (s, 5H, C_5H_5); 3.66–2.34 (m, 3H, CH + CH_2). ^{31}P NMR: 94.5 (dd, J_{PP} = 58.6 Hz, J_{RhP} = 219.7 Hz); 63.3 (dd, J_{PP} = 58.9 Hz, J_{RhP} = 217.3 Hz). ^{13}C NMR: 136.8–127.2 (m, C_6H_5); 85.4 (s, C_5H_5); 48.3, 37.0, 29.1 (m, CH + CH_2). Anal. Found: C, 68.62; H, 5.27. Calcd for $C_{37}H_{33}P_2Rh$: C, 69.17; H, 5.18.

(η^5-C_5H_5)Rh(cycphos) (1f). ^{1}H NMR: 7.17 (m, 20H, C_6H_5); 4.91 (s, 5H, C_5H_5); 2.65–0.46 (m, 14H, CH + CH_2 + C_6H_{11}). ^{31}P NMR: 87.9 (dd, J_{PP} = 53.7 Hz, J_{RhP} = 214.8 Hz); 66.2 (dd, J_{PP} = 53.7 Hz, J_{RhP} = 214.8 Hz). ^{13}C NMR: 143.6–127.3 (m, C_6H_5); 85.4 (s, C_5H_5); 46.5, 36.1, 26.7 (m, CH + CH_2 + C_6H_{11}). Anal. Found: C, 69.43; H, 6.31. Calcd for $C_{37}H_{39}P_2Rh$: C, 68.52; H, 6.06.

General Procedure for the Preparation of (η^5-C_9H_7)Rh(L_2) Complexes. A solution of 0.3 g (1.33 mmol) of (η^5-C_9H_7)Rh(C_2H_4)$_2$ and of a equimolar amount of the appropriate diphosphine was stirred at room temperature for 5 h in 20 mL of toluene. The solvent was then removed under reduced pressure, and 20 mL of *n*-hexane was added. The microcrystalline compounds were filtered off, washed with *n*-hexane, and dried in vacuo. Recrystallization was from CH_2Cl_2/*n*-hexane. Yields are in the range 70–90%.

Elemental analyses and NMR parameters (δ, $C_6D_5CD_3$) are as follows.

(η^5-C_9H_7)Rh(chiraphos) (3a). ^{1}H NMR: 7.44 (m, 24H, C_6H_5 + C_6H_4); 5.95 (q, J = 2.4 Hz, 1H (ind)); 5.05 (bs, 2H (ind)); 1.59 (m, 2H, CH); 0.74 (dd, J_{HH} = 6.4 Hz, J_{PH} = 10.7 Hz, 6H, CH_3). ^{31}P NMR: 79.9 (d, J_{RhP} = 214.8 Hz). ^{13}C NMR: 136.8–119.9 (m, C_6H_5); 95.2 (s, C(ind)); 76.5 (s, C(ind)); 73.7 (s, C(ind)); 38.5–35.5 (m, CH); 15.5–13.0 (m, CH_3). Anal. Found: C, 68.90; H, 5.51. Calcd for $C_{37}H_{35}P_2Rh$: C, 68.95; H, 5.47.

(η^5-C_9H_7)Rh(cypenphos) (3b). ^{1}H NMR: 7.21 (m, 24H, C_6H_5 + C_6H_4); 6.01 (q, J = 2.4 Hz, 1H (ind)); 5.07 (bs, 2H (ind)); 2.09–0.86 (m, 8H, CH + CH_2). ^{31}P NMR: 55.2 (d, J_{RhP} = 218.3 Hz). ^{13}C NMR: 141.6–115.2 (m, C_6H_5); 94.5 (s, C(ind)); 74.6 (s, C (ind));

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Table V. Atomic Coordinates and Isotropic Displacement Parameters (or Equivalent Isotropic Displacement Parameters)[a] for $(R)_C,(S)_{Rh}$-[(η^5-C_9H_7)Rh(CH_3)(prophos)][BPh_4]

atom	x	y	z	B (Å²)	atom	x	y	z	B (Å²)
Rha	−0.05647(6)	0.00000	−0.33471(3)	3.10(2)*	C124b	0.2183(4)	0.6567(8)	0.0139(3)	5.1(3)
P1a	−0.0329(2)	−0.0941(3)	−0.4020(1)	3.61(9)*	C125b	0.3111(4)	0.6659(8)	0.0332(3)	5.8(3)
P2a	0.0105(2)	0.1472(3)	−0.3687(1)	3.11(8)*	C126b	0.3665(4)	0.5698(8)	0.0400(3)	5.3(3)
C1a	0.0820(8)	−0.038(1)	−0.3063(4)	5.4(4)*	C211b	0.5916(6)	0.1254(8)	0.1413(2)	4.1(3)
C2a	0.0305(8)	0.000(1)	−0.4377(4)	4.1(3)*	C212b	0.6413(6)	0.0558(8)	0.1134(2)	5.3(3)
C3a	0.0884(8)	0.090(1)	−0.4100(4)	3.2(3)*	C213b	0.6734(6)	−0.0487(8)	0.1303(2)	6.0(4)
C4a	0.1305(9)	0.172(1)	−0.4433(4)	5.2(4)*	C214b	0.6560(6)	−0.0836(8)	0.1750(2)	6.0(4)
C5a	−0.160(1)	−0.106(2)	−0.3016(6)	5.8(5)*	C215b	0.6063(6)	−0.0140(8)	0.2029(2)	6.0(3)
C6a	−0.100(1)	−0.056(2)	−0.2673(5)	5.4(5)*	C216b	0.5742(6)	0.0905(8)	0.1860(2)	5.7(3)
C7a	−0.113(1)	0.061(2)	−0.2697(5)	5.0(5)*	C221b	0.5759(4)	0.3607(7)	0.1625(3)	3.6(3)
C8a	−0.1889(9)	0.083(1)	−0.3050(4)	3.9(4)*	C222b	0.5224(4)	0.4579(7)	0.1655(3)	4.0(3)
C9a	−0.236(1)	0.181(1)	−0.3185(5)	5.5(5)*	C223b	0.5552(4)	0.5451(7)	0.1953(3)	5.2(3)
C10a	−0.308(1)	0.177(2)	−0.3507(7)	6.7(6)*	C224b	0.6414(4)	0.5350(7)	0.2220(3)	5.6(3)
C11a	−0.340(1)	0.077(2)	−0.3702(6)	7.4(7)*	C225b	0.6949(4)	0.4378(7)	0.2189(3)	5.8(3)
C12a	−0.293(1)	−0.023(2)	−0.3611(5)	6.0(5)*	C226b	0.6621(4)	0.3506(7)	0.1891(3)	5.6(3)
C13a	−0.2175(9)	−0.021(1)	−0.3259(4)	4.3(4)*	B1	0.945(1)	0.360(1)	0.8764(5)	4.0(3)
C111a	0.0351(6)	−0.2237(8)	−0.3959(3)	4.6(3)	CA2	0.9618(4)	0.1414(7)	0.8650(2)	3.7(3)
C112a	0.0300(6)	−0.2887(8)	−0.3557(3)	5.3(3)	CA3	1.0051(4)	0.0445(7)	0.8501(2)	4.4(3)
C113a	0.0802(6)	−0.3890(8)	−0.3501(3)	8.0(4)	CA4	1.0858(4)	0.0533(7)	0.8270(2)	5.1(3)
C114a	0.1355(6)	−0.4245(8)	−0.3847(3)	7.8(4)	CA5	1.1231(4)	0.1589(7)	0.8186(2)	4.5(3)
C115a	0.1406(6)	−0.3595(8)	−0.4249(3)	7.9(4)	CA6	1.0797(4)	0.2558(7)	0.8335(2)	4.1(3)
C116a	0.0904(6)	−0.2591(8)	−0.4305(3)	6.2(3)	CA1	0.9991(4)	0.2470(7)	0.8566(2)	3.3(2)
C121a	−0.1385(5)	−0.1394(7)	−0.4381(2)	3.7(3)	CA8	0.8093(5)	0.3363(7)	0.8073(2)	4.8(3)
C122a	−0.1821(5)	−0.2393(7)	−0.4267(2)	4.2(3)	CA9	0.7165(5)	0.3296(7)	0.7880(2)	5.2(3)
C123a	−0.2687(5)	−0.2686(7)	−0.4498(2)	5.8(3)	CA10	0.6442(5)	0.3324(7)	0.8171(2)	4.6(3)
C124a	−0.3117(5)	−0.1981(7)	−0.4844(2)	5.5(3)	CA11	0.6647(5)	0.3419(7)	0.8655(2)	4.8(3)
C125a	−0.2682(5)	−0.0983(7)	−0.4958(2)	5.9(3)	CA12	0.7576(5)	0.3486(7)	0.8848(2)	4.8(3)
C126a	−0.1816(5)	−0.0690(7)	−0.4726(2)	4.7(3)	CA7	0.8299(5)	0.3458(7)	0.8557(2)	3.2(2)
C211a	0.0766(5)	0.2430(7)	−0.3293(3)	3.5(2)	CA14	1.0741(6)	0.5141(8)	0.8760(3)	6.3(3)
C212a	0.1738(5)	0.2529(7)	−0.3258(3)	4.5(3)	CA15	1.1116(6)	0.6160(8)	0.8626(3)	9.1(5)
C213a	0.2190(5)	0.3300(7)	−0.2947(3)	4.7(3)	CA16	1.0592(6)	0.6863(8)	0.8311(3)	8.1(4)
C214a	0.1670(5)	0.3972(7)	−0.2670(3)	4.9(3)	CA17	0.9694(6)	0.6546(8)	0.8130(3)	6.3(4)
C215a	0.0697(5)	0.3873(7)	−0.2704(3)	4.9(3)	CA18	0.9319(6)	0.5526(8)	0.8263(3)	4.5(3)
C216a	0.0245(5)	0.3102(7)	−0.3016(3)	4.0(3)	CA13	0.9843(6)	0.4824(8)	0.8579(3)	4.0(3)
C221a	−0.0669(5)	0.2388(5)	−0.4053(3)	2.9(2)	CA20	0.9221(5)	0.4519(6)	0.9579(3)	4.9(3)
C222a	−0.1536(5)	0.1993(5)	−0.4247(3)	3.5(3)	CA21	0.9294(5)	0.4560(6)	1.0067(3)	6.5(4)
C223a	−0.2112(5)	0.2679(5)	−0.4547(3)	4.3(3)	CA22	0.9732(5)	0.3686(6)	1.0329(3)	5.9(3)
C224a	−0.1819(5)	0.3760(5)	−0.4653(3)	4.9(3)	CA23	1.0099(5)	0.2772(6)	1.0103(3)	4.7(3)
C225a	−0.0951(5)	0.4155(5)	−0.4459(3)	4.1(3)	CA24	1.0027(5)	0.2732(6)	0.9615(3)	3.8(3)
C226a	−0.0376(5)	0.3469(5)	−0.4159(3)	4.0(3)	CA19	0.9588(5)	0.3605(6)	0.9353(3)	3.7(3)
Rhb	0.37737(6)	0.2390(1)	0.10424(3)	3.28(2)*	B2	0.5299(9)	0.524(1)	0.6283(5)	3.8(3)
P1b	0.3983(2)	0.3385(3)	0.0385(1)	3.40(8)*	CA26	0.7184(5)	0.4954(7)	0.6333(2)	4.5(3)
P2b	0.5346(2)	0.2522(3)	0.1204(1)	3.35(8)*	CA27	0.8085(5)	0.5056(7)	0.6560(2)	4.7(3)
C1b	0.4079(9)	0.091(1)	0.0697(4)	5.0(4)*	CA28	0.8223(5)	0.5577(7)	0.6997(2)	4.5(3)
C2b	0.5205(7)	0.385(1)	0.0425(4)	3.5(3)*	CA29	0.7459(5)	0.5995(7)	0.7207(2)	4.8(3)
C3b	0.5838(7)	0.294(1)	0.0660(4)	3.4(3)*	CA30	0.6557(5)	0.5893(7)	0.6981(2)	4.3(3)
C4b	0.6889(7)	0.332(1)	0.0725(4)	4.0(3)*	CA25	0.6420(5)	0.5372(7)	0.6544(2)	3.0(2)
C5b	0.2250(8)	0.250(2)	0.1096(5)	5.7(4)*	CA32	0.3830(6)	0.6146(7)	0.6636(3)	5.4(3)
C6b	0.256(1)	0.147(2)	0.1261(6)	5.3(5)*	CA33	0.3338(6)	0.7074(7)	0.6781(3)	7.9(4)
C7b	0.320(1)	0.164(1)	0.1665(5)	4.7(4)*	CA34	0.3698(6)	0.8155(7)	0.6739(3)	8.6(5)
C8b	0.3177(9)	0.283(1)	0.1781(5)	4.0(4)*	CA35	0.4549(6)	0.8309(7)	0.6551(3)	7.7(4)
C9b	0.353(1)	0.346(2)	0.2160(5)	6.2(5)*	CA36	0.5041(6)	0.7381(7)	0.6406(3)	6.2(3)
C10b	0.333(1)	0.460(2)	0.2165(7)	7.0(6)*	CA31	0.4681(6)	0.6299(7)	0.6449(3)	4.1(3)
C11b	0.279(1)	0.512(2)	0.1808(8)	7.5(6)*	CA38	0.5669(5)	0.4281(6)	0.5475(2)	3.8(3)
C12b	0.245(1)	0.453(2)	0.1431(6)	6.3(5)*	CA39	0.5691(5)	0.4263(6)	0.4989(2)	4.1(3)
C13b	0.2599(0)	0.337(1)	0.1412(5)	4.1(4)*	CA40	0.5328(5)	0.5165(6)	0.4718(2)	4.7(3)
C111b	0.3757(4)	0.2617(7)	−0.0164(3)	3.5(2)	CA41	0.4944(5)	0.6086(6)	0.4932(2)	5.5(3)
C112b	0.2906(4)	0.2050(7)	−0.0246(3)	3.9(3)	CA42	0.4923(5)	0.6104(6)	0.5417(2)	4.4(3)
C113b	0.2686(4)	0.1480(7)	−0.0667(3)	4.5(3)	CA37	0.5286(5)	0.5202(6)	0.5688(2)	3.5(2)
C114b	0.3318(4)	0.1476(7)	−0.1007(3)	4.3(3)	CA44	0.4291(5)	0.3359(7)	0.6143(2)	4.5(3)
C115b	0.4169(4)	0.2042(7)	−0.0925(3)	4.8(3)	CA45	0.3999(5)	0.2293(7)	0.6269(2)	4.6(3)
C116b	0.4389(4)	0.2612(7)	−0.0504(3)	4.6(3)	CA46	0.4290(5)	0.1861(7)	0.6712(2)	6.2(4)
C121b	0.3291(4)	0.4644(8)	0.0275(3)	3.7(3)	CA47	0.4873(5)	0.2497(7)	0.7028(2)	4.8(3)
C122b	0.2364(4)	0.4552(8)	0.0082(3)	6.9(4)	CA48	0.5165(5)	0.3564(7)	0.6902(2)	4.1(3)
C123b	0.1810(4)	0.5513(8)	0.0014(3)	6.6(4)	CA43	0.4874(5)	0.3995(7)	0.6459(2)	3.7(3)

[a] Equivalent isotropic *B* (marked with an asterisk) defined as one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor.

71.04 (s, C (ind)); 49.7, 31.2, 23.5 (m, CH + CH_2). Anal. Found: C, 70.15; H, 5.51. Calcd for $C_{38}H_{35}P_2Rh$: C, 69.52; H, 5.37.

(η^5-C_9H_7)Rh(renorphos) (3c). ^{1}H NMR: 6.94 (m, 24H, C_6H_5 + C_6H_4); 5.94 (q, J = 2.44 Hz, 1H (ind)); 5.13 (s, 1H (ind)); 4.97 (s, 1H (ind)); 2.12–0.75 (m, 10H, CH + CH_2). ^{31}P NMR: 58.7 (dd, J_{PP} = 51.3 Hz, J_{RhP} = 224.6 Hz); 49.5 (dd, J_{PP} = 51.3 Hz, J_{RhP} = 222.2 Hz). ^{13}C NMR: 139.5–118.9 (m, C_6H_5); 92.8 (s, C(ind)); 75.6 (s, C (ind)); 72.3 (s, C (ind)); 46.2, 37.2 (m, CH + CH_2). Anal. Found: C, 69.78; H, 5.50. Calcd for $C_{40}H_{37}P_2Rh$: C, 70.38; H, 5.46.

(η^5-C_9H_7)Rh(prophos) (3d). ^{1}H NMR: 7.28 (m, 24H, C_6H_5 + C_6H_4); 6.0 (q, J = 2.44 Hz, 1H (ind)); 5.19 (bs, 2H (ind)); 2.20–1.50 (m, 3H, CH + CH_2); 0.82 (dd, J_{HH} = 6.4 Hz, J_{PH} = 11.3 Hz, 3H, CH_3). ^{31}P NMR: 83.2 (dd, J_{PP} = 46.4 Hz, J_{RhP} = 219.7 Hz); 65.2 (dd, J_{PP} = 46.4 Hz, J_{RhP} = 219.7 Hz). ^{13}C NMR: 144.7–116.2 (m, C_6H_5); 95.1 (s, C (ind)); 74.7 (s, C (ind)); 72.6 (s, C (ind));

38.9–32.9 (m, CH + CH_2); 16.6 (bs, CH_3). Anal. Found: C, 68.97; H, 5.40. Calcd for $C_{36}H_{33}P_2Rh$: C, 68.57; H, 5.27.

(η^5-C_9H_7)Rh(phenphos) (3e). ^{1}H NMR: 6.89 (m, 29H, C_6H_5 + C_6H_4); 5.88 (q, J = 2.4 Hz, 1H (ind)); 5.12 (s, 1H (ind)); 4.99 (s, 1H (ind)); 3.13–1.84 (m, 3H, CH + CH_2). ^{31}P NMR: 90.4 (dd, J_{PP} = 53.7 Hz, J_{RhP} = 222.2 Hz); 57.6 (dd, J_{PP} = 53.7 Hz, J_{RhP} = 217.3 Hz). ^{13}C NMR: 140.8–117.1 (m, C_6H_5); 92.4 (s, C (ind)); 78.3 (s, C (ind)); 72.5 (s, C (ind)); 46.3–27.1 (m, CH + CH_2). Anal. Found: C, 71.13; H, 5.17. Calcd for $C_{41}H_{35}P_2Rh$: C, 71.10; H, 5.09.

(η^5-C_9H_7)Rh(cycphos) (3f). ^{1}H NMR: 6.82 (m, 24H, C_6H_5 + C_6H_4); 5.80 (q, J = 2.4 Hz, 1H (ind)); 5.09 (s, 1H (ind)); 5.00 (s, 1H (ind)); 2.32–0.61 (m, 14H, CH + CH_2 + C_6H_{11}). ^{31}P NMR: 83.7 (dd, J_{PP} = 51.3 Hz, J_{RhP} = 214.8 Hz); 61.0 (dd, J_{PP} = 51.3 Hz, J_{RhP} = 217.4 Hz). ^{13}C NMR: 141.5–117.3 (m, C_6H_5); 92.4 (s, C (ind)); 77.8 (s, C (ind)), 71.6 (s, C (ind)); 48.4–22.3 (m, CH + CH_2 + C_6H_{11}). Anal. Found: C, 71.09; H, 6.14. Calcd for $C_{41}H_{41}P_2Rh$: C, 70.49; H, 5.91.

General Procedure for the Reaction of (η^5-C_5H_5)Rh(L_2) (1) and (η^5-C_9H_7)Rh(L_2) (3) Complexes with CH_3I. In general the reactions were carried out directly in an NMR tube. We report in detail the preparation of the complex [(η^5-C_9H_7)Rh(prophos)(CH_3)]BPh_4 (**4d**), for which the X-ray structure was determined.

Preparation of [(η^5-C_9H_7)Rh(prophos)(CH_3)]BPh_4 (4d). A solution of 1 g (1.6 mmol) of (η^5-C_9H_7)Rh(prophos) (**3d**) and 1.5 mL of CH_3I (excess) was stirred at room temperature in 20 mL of dichloromethane for 30 min. The solvent was then removed under reduced pressure and the residue treated with 20 mL of *n*-hexane. After filtration, the yellow microcrystalline compound was washed three times with 10 mL of *n*-hexane and dried in vacuo. The compound so obtained was treated with an excess of $NaBPh_4$ in 20 mL of methanol at room temperature for 24 h. The methanol was removed under reduced pressure, the residue dissolved in 30 mL of dichloromethane, 30 mL of water added, and the mixture stirred for 2 h. The organic layer was separated, dried on Na_2SO_4, filtered, and concentrated. Addition of *n*-hexane induced precipitation of a yellow crystalline product, which was filtered and washed with 20 mL of *n*-hexane; yield 1.2 g (80%). ^{1}H NMR (δ, CD_2Cl_2): 7.55–6.38 (m, 44H, C_6H_5); 5.99 (m, 1H, H (ind)); 5.32 (m, 2H, H (ind)); 3.16–1.50 (m, 3H, CH + CH_2); 1.02 (dd, 3H, CH_3 (prophos), J_{HH} = 6.3 Hz, J_{PH} = 12.7 Hz); –0.04 (dt, 3H, CH_3, J = 2.5 and 5.9 Hz). ^{31}P NMR (δ, CD_2Cl_2): 82.32 (dd, J_{PP} = 29.3 Hz, J_{RhP} = 144.1 Hz); 53.28 (dd, J_{PP} = 29.3 Hz, J_{RhP} = 146.5 Hz). ^{13}C NMR (δ, CD_2Cl_2): 136.5–121.5 (m, C_6H_5); 117.2 (s, C (ind)); 112.3 (s, C (ind)); 104.4 (s, C (ind)); 80.0 (m, C (ind)); 30.5 (m, CH + CH_2); 15.7 (m, CH_3 (prophos)); –0.9 (m, CH_3). Anal. Found: C, 75.70; H, 5.96. Calcd for $C_{61}H_{56}BP_2Rh$: C, 75.94; H, 5.85.

Elemental analyses and NMR data for [(η^5-C_5H_5)Rh(L_2)(CH_3)]I and for [(η^5-C_9H_7)Rh(L_2)(CH_3)]I complexes (δ, CD_2Cl_2) are as follows.

[(η^5-C_5H_5)Rh(chiraphos)(CH_3)]I (2a). ^{1}H NMR: 7.47 (m, 30H, C_6H_5); 5.37 (t, J = 1.4 Hz, 5H, C_5H_5); 3.02, 1.86 (m, 2H, CH); 1.18 (dd, J_{HH} = 6.8 Hz, J_{PH} = 12.7 Hz, 3H, CH_3); 0.93 (dd, J_{HH} = 6.8 Hz, J_{PH} = 13.7 Hz, 3H, CH_3); –0.35 (dt, J = 2.4 Hz, J = 6.8 Hz, 3H, CH_3). ^{31}P NMR: 82.7 (dd, J_{PP} = 39.1 Hz, J_{RhP} = 139.2 Hz); 73.7 (dd, J_{PP} = 39.1 Hz, J_{RhP} = 141.6 Hz). ^{13}C NMR: 135.3–127.7 (m, C_6H_5); 94.0 (s, C_5H_5); 45.2, 29.1 (m, CH); 12.5 (m, CH_3); –9.5 (m, CH_3). Anal. Found: C, 54.95; H, 5.01. Calcd for $C_{34}H_{36}P_2IRh$: C, 55.45; H, 4.92.

[(η^5-C_5H_5)Rh(cypenphos)(CH_3)]I (2b). ^{1}H NMR: 7.60 (m, 20H, C_6H_5); 5.47 (t, J = 1.4 Hz, 5H, C_5H_5); 3.43–1.00 (m, 8H, CH + CH_2); 0.22 (dt, J = 1.9 Hz, J = 4.4 Hz, 3H, CH_3). ^{31}P NMR: 61.6 (dd, J_{PP} = 43.9 Hz, J_{RhP} = 141.6 Hz); 44.2 (J_{PP} = 43.9 Hz, J_{RhP} = 146.5 Hz). ^{13}C NMR: 135.0–126.1 (m, C_6H_5); 93.3 (s, C_5H_5); 47.3–22.7 (m, CH + CH_2); –10.9 (m, CH_3). Anal. Found: C, 55.86; H, 4.91. Calcd for $C_{35}H_{36}P_2IRh$: C, 56.17; H, 4.85.

[(η^5-C_5H_5)Rh(renorphos)(CH_3)]I (2c). ^{1}H NMR: 7.74 (m, 20H, C_6H_5); 5.54 (t, J = 1.4 Hz, 5H, C_5H_5); 5.45 (t, J = 1.4 Hz); 3.20–1.03 (m, 10H, CH + CH_2); 0.72 (m, 3H, CH_3); 0.29 (m, 3H, CH_3). ^{31}P NMR (minor diastereomer): 64.6 (dd, J_{PP} = 43.9 Hz, J_{RhP} = 144.0 Hz); 38.5 (dd, J_{PP} = 43.9 Hz, J_{RhP} = 148.9 Hz). ^{31}P NMR (major diastereomer): 53.4 (dd, J_{PP} = 43.9 Hz, J_{RhP} = 144.1 Hz); 49.3 (dd, J_{PP} = 43.9 Hz, J_{RhP} = 148.9 Hz). ^{13}C NMR: 135.6–129.3 (m, C_6H_5); 93.5 (s, C_5H_5); 87.5 (s, C_5H_5); 47.1–21.3 (m, CH + CH_2); –8.2 (m, CH_3); –12.40 (m, CH_3). Anal. Found: C, 56.80, H, 5.67. Calcd for $C_{37}H_{38}P_2IRh$: C, 57.38; H, 4.94.

[(η^5-C_5H_5)Rh(prophos)(CH_3)]I (2d). ^{1}H NMR: 7.56 (m, 20H, C_6H_5); 5.47 (t, J = 1.4 Hz, 5H, C_5H_5); 3.53–2.97 (m, 3H, CH + CH_2); 1.17 (dd, J_{HH} = 5.4 Hz, J_{PH} = 12.2 Hz, 3H, CH_3); –0.15 (J = 2.4 Hz, J = 5.8 Hz). ^{31}P NMR: 85.3 (dd, J_{PP} = 34.2 Hz, J_{RhP} = 141.6 Hz); 59.3 (dd, J_{PP} = 34.2 Hz, J_{RhP} = 144.0 Hz). ^{13}C NMR: 135.2–128.3 (m, C_6H_5); 94.0 (s, C_5H_5); 37.0–32.6 (m, CH + CH_2); 15.7 (m, CH_3); –9.8 (m, CH_3). Anal. Found: C, 54.49; H, 4.75. Calcd for $C_{33}H_{34}P_2IRh$: C, 54.87; H, 5.74.

[(η^5-C_5H_5)Rh(phenphos)(CH_3)]I (2e). ^{1}H NMR: 7.59 (m, 25H, C_6H_5); 5.53 (s, 5H, C_5H_5); 5.00 (s, 5H, C_5H_5); 4.30–2.78 (m, 3H, CH + CH_2); 0.32 (m, 3H, CH_3); 0.08 (m, 3H, CH_3). ^{31}P NMR (major diastereomer): 87.5 (dd, J_{PP} = 36.6 Hz, J_{RhP} = 141.6 Hz); 54.0 (dd, J_{PP} = 36.6 Hz, J_{RhP} = 141.6 Hz). ^{31}P NMR (minor diastereomer): 75.7 (dd, J_{PP} = 36.6 Hz, J_{RhP} = 144.0 Hz); 66.06 (dd, J_{PP} = 36.6 Hz, J_{RhP} = 144.0 Hz). ^{13}C NMR: 135.6–125.1 (m, C_6H_5); 93.7 (s, C_5H_5); 87.0 (s, C_5H_5); 43.6–32.5 (m, CH + CH_2); –7.85 (m, CH_3); –9.64 (m, CH_3). Anal. Found: C, 59.40; H, 4.69. Calcd for $C_{38}H_{36}P_2IRh$: C, 58.18; H, 4.62.

[(η^5-C_5H_5)Rh(cycphos)(CH_3)]I (2f). ^{1}H NMR: 7.61 (m, 20H, C_6H_5); 5.48 (s, 5H, C_5H_5); 3.11–0.65 (m, 14H, CH + CH_2 + C_6H_{11}); –0.26 (dt, J = 1.9 Hz, J = 5.4 Hz, 3H, CH_3). ^{31}P NMR: 85.2 (dd, J_{PP} = 36.6 Hz, J_{RhP} = 141.6 Hz); 57.5 (dd, J_{PP} = 36.6 Hz, J_{RhP} = 146.5 Hz). ^{13}C NMR: 135.0–129.9 (m, C_6H_5); 94.2 (s, C_5H_5); 37.5–26.3 (m, CH + CH_2 + C_6H_{11}); –8.66 (m, CH_3). Anal. Found: C, 57.34; H, 5.34. Calcd for $C_{38}H_{42}P_2IRh$: C, 57.73; H, 5.36.

[(η^5-C_9H_7)Rh(chiraphos)(CH_3)]I (4a). ^{1}H NMR: 7.52 (m, 24H, C_6H_5 + C_6H_4); 5.84 (s, 1H (ind)); 5.63 (bs 2H (ind)); 2.95, 1.80 (m, 2H, CH); 1.19 (dd, J_{HH} = 7.3 Hz, J_{PH} = 12.7 Hz, 3H, CH_3); 0.96 (dd, J_{HH} = 6.3 Hz, J_{PH} = 13.7 Hz); –0.45 (dt, J = 1.9 Hz, J = 4.9 Hz, 3H, CH_3). ^{31}P NMR: 83.1 (dd, J_{PP} = 34.2 Hz, J_{RhP} = 146.5 Hz); 67.7 (dd, J_{PP} = 34.2 Hz, J_{RhP} = 146.5 Hz). ^{13}C NMR: 135.2–121.9 (m, C_6H_5); 114.8 (s, C(ind)); 112.7 (s, C (ind)); 103.1 (s, C (ind)); 82.2 (m, C (ind)); 42.3, 36.3 (m, CH); 15.4, 12.7 (m, CH_3); 1.14 (m, CH_3). Anal. Found: C, 55.99; H, 4.91. Calcd for $C_{38}H_{38}P_2IRh$: C, 55.35; H, 4.64.

[(η^5-C_9H_7)Rh(cypenphos)(CH_3)]I (4b). ^{1}H NMR: 7.56 (m, 24H, C_6H_5 + C_6H_4); 6.01–5.75 (m, 3H (ind)); 3.21–1.87 (m, 8H, CH + CH_2); 0.40 (m, 3H, CH_3). ^{31}P NMR: 60.81 (dd, J_{PP} = 41.5 Hz; J_{RhP} = 144.0 Hz); 40.12 (dd, J_{PP} = 41.5 Hz J_{RhP} = 151.4 Hz). ^{13}C NMR: 134.4–121.2 (m, C_6H_5); 117.6 (s, C (ind)); 111.8 (s, C (ind)); 104.5 (s, C (ind)); 81.2 (m, C (ind)); 47.3, 24.3 (m, CH + CH_2); –2.8 (m, CH_3). Anal. Found: C, 57.94; H, 4.98. Calcd for $C_{39}H_{38}P_2IRh$: C, 58.66; H, 4.80.

[(η^5-C_9H_7)Rh(renorphos)(CH_3)]I (4c). ^{1}H NMR: 7.63 (m, 24H, C_6H_5 + C_6H_4); 6.11–5.74 (m, 3H (ind)); 2.78–1.26 (m, 10H, CH + CH_2); 0.77, 0.21 (m, 3H, CH_3). ^{31}P NMR (major diastereomer): 59.2 (dd, J_{PP} = 41.5 Hz, J_{RhP} = 144.0 Hz); 37.3 (dd, J_{PP} = 41.5 Hz, J_{RhP} = 151.4 Hz). ^{31}P NMR (minor diastereomer): 50.21 (dd, J_{PP} = 39.1 Hz, J_{RhP} = 146.5 Hz); 44.7 (dd, J_{PP} = 39.1 Hz, J_{RhP} = 151.4 Hz). ^{13}C NMR: 136.4–121.5 (m, C_6H_5); 119.5 (s, C (ind)); 117.7 (s, C (ind)); 111.8 (s, C (ind)); 105.8 (s, C (ind)); 105.0 (s, C (ind)); 80.5 (m, C (ind)); 79.3 (m, C (ind)); 77.7 (m, C (ind)); 50.5–34.5 (m, CH + CH_2); 1.2 (m, CH_3); –4.4 (m, CH_3). Anal. Found: C, 59.27; H, 4.93. Calcd for $C_{41}H_{40}P_2$-IRh: C, 59.72; H, 4.89.

[(η^5-C_9H_7)Rh(phenphos)(CH_3)]I (4e). ^{1}H NMR: 7.62 (m, 29H, C_6H_5 + C_6H_4); 6.12 (s, 1H (ind)); 5.74 (s, 2H (ind)); 4.04–2.61 (m, 3H, CH + CH_2); 0.38, 0.08 (m, 3H, CH_3). ^{31}P NMR (major diastereomer): 84.4 (dd, J_{PP} = 34.2 Hz, J_{RhP} = 144.0 Hz); 48.9 (dd, J_{PP} = 34.2 Hz, J_{RhP} = 148.9 Hz). ^{31}P NMR (minor diastereomer): 73.3 (dd, J_{PP} = 34.2 Hz, J_{RhP} = 148.9 Hz); 64.4 (dd, J_{PP} = 34.2 Hz, J_{RhP} = 144.0 Hz). ^{13}C NMR: 135.8–121.6 (m, C_6H_5); 116.9 (s, C (ind)); 112.0 (s, C (ind)); 104.7 (s, C (ind)); 81.1 (s, C (ind)); 43.2, 32.0 (m, CH + CH_2); 1.2 (m, CH_3). Anal. Found: C, 59.55; H, 4.80. Calcd for $C_{42}H_{40}P_2IRh$: C, 60.30; H, 4.81.

[(η^5-C_9H_7)Rh(cycphos)(CH_3)I (4f). ^{1}H NMR: 7.59 (m, 24H,

C_6H_5 + C_6H_4); 6.03–5.70 (m, 3H (ind)); 3.29–0.53 (m, 14H, CH + CH_2 + C_6H_{11}); –0.27 (dt, J = 1.9 Hz, J = 5.4 Hz, 3H, CH_3). ^{31}P NMR: 83.1 (dd, J_{PP} = 31.7 Hz, J_{RhP} = 144.2 Hz); 52.2 (dd, J_{PP} = 31.7 Hz, J_{RhP} = 146.5 Hz). ^{13}C NMR: 134.4–121.9 (m, C_6H_5); 116.2 (s, C (ind)); 112.2 (s, C (ind)); 81.5 (s, C (ind)); 41.5, 28.0, 25.5 (m, CH + CH_2 + C_6H_{11}); 1.0 (m, CH_3). Anal. Found: C, 59.51; H, 5.38. Calcd for $C_{42}H_{44}P_2IRh$: C, 60.01; H, 5.27.

Apparatus and Procedure for the Electrochemical Measurements. All experiments were performed on anhydrous, deoxygenated AN solutions with 0.2 M TEAP as the supporting electrolyte, using a conventional three-electrode liquid-jacketed cell. Cyclic voltammetry measurements were performed with an Amel 551 potentiostat modulated by an Amel 566 function generator, and the recording device was a Hewlett-Packard 7090 A measurement plotting system. The working electrode was a planar platinum microelectrode (ca. 0.3 mm^2) surrounded by a platinum spiral counter electrode.

Controlled-potential electrolyses were performed with an Amel 552 potentiostat linked to an Amel 731 digital integrator. The working electrode was a mercury pool, and the counter electrode was external, the connection being made through an appropriate salt bridge.

In all cases silver/0.1 M silver perchlorate in acetonitrile, separated from the test solution by 0.2 M TEAP in AN solution sandwiched between two fritted disks, was used as the reference electrode. Compensation for iR drop was achieved by positive feedback. Ferrocene was added at the end of each experiment as the internal reference. All potentials are referred to the ferrocenium/ferrocene couple.

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Supplementary Material Available: Listings of H atom positional parameters, anisotropic thermal parameters, and additional bond distances and angles for $(R)_C,(S)_{Rh}$-[(η^5-C_9H_7)Rh($Ph_2PCH(CH_3)CH_2PPh_2$)(CH_3)]BPh_4 (12 pages). Ordering information is given on any current masthead page.

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